

WHAT IS CLAIMED IS:

1. A monovinylarene/conjugated diene block copolymer, comprising:
a random (conjugated diene_x/monovinylarene_y)_m block, wherein x is about 2.5
5 wt% to about 10 wt%, y is from about 90 wt% to about 97.5 wt%, and x + y is about 97.5
wt% to 100 wt%; and
a (conjugated diene)_n block;
wherein n is from about 20 wt% to about 30 wt%, m is from about 70 wt% to
about 80 wt%, and m + n is from about 90 wt% to 100 wt%.
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2. The monovinylarene/conjugated diene block copolymer of claim 1, wherein x is
about 5 wt% to about 10 wt%.
3. The monovinylarene/conjugated diene block copolymer of claim 1, wherein y is
15 about 90 wt% to about 95 wt%.
4. The monovinylarene/conjugated diene block copolymer of claim 1, wherein n is
about 25 wt% and m is about 75 wt%.
- 20 5. The monovinylarene/conjugated diene block copolymer of claim 1, wherein the
T_g is at least about 10°C less than the T_g of a reference polymer differing only in x being
about 0 wt% and y being about 100 wt%.
6. The monovinylarene/conjugated diene block copolymer of claim 5, wherein the
25 T_g is at least about 20°C less than the T_g of the reference polymer.
7. The monovinylarene/conjugated diene block copolymer of claim 6, wherein the
T_g is at least about 30°C less than the T_g of the reference polymer.

8. The monovinylarene/conjugated diene block copolymer of claim 1, further comprising a monovinylarene/conjugated diene block.

9. The monovinylarene/conjugated diene block copolymer of claim 1, further comprising a monovinylarene block.

10. An article, comprising the monovinylarene/conjugated diene block copolymer of claim 1.

11. The article of claim 10, wherein the article is a shrink film.

12. A method of preparing a monovinylarene/conjugated diene block copolymer having a low T_g , comprising:

(a) charging a monovinylarene monomer, a conjugated diene monomer, an initiator, and a randomizer, allowing polymerizing to occur, to produce a random (conjugated diene_x/monovinylarene_y)_m block;

(b) charging a monovinylarene monomer, a conjugated diene monomer, and an initiator, allowing polymerization to occur, to produce a monovinylarene/conjugated diene block;

(c) charging a conjugated diene monomer, and allowing polymerization to occur, to produce a (conjugated diene)_n block; and

(c) charging the reaction mixture with a coupling agent, to form monovinylarene/conjugated diene block copolymer.

13. The method of claim 12, wherein x is about 2.5 wt% to about 10 wt%, y is from about 90 wt% to about 97.5 wt%, and x + y is about 97.5 wt% to 100 wt%.

14. The method of claim 12, wherein n is from about 20 wt% to about 30 wt%, m is from about 70 wt% to about 80 wt%, and m + n is from about 90 wt% to 100 wt%.

15. A monovinylarene/conjugated diene block copolymer, produced according to the method of claim 12.

16. A method of preparing a monovinylarene/conjugated diene block copolymer having a low T_g , comprising:

(a) charging an initiator and a monovinylarene monomer and allowing polymerization to occur, to produce a monovinylarene block;

(b) charging a randomizer, an initiator, and a conjugated diene/monovinylarene monomer mixture and allowing polymerization to occur, to produce a random (conjugated diene_x/monovinylarene_y)_m block;

(c) charging a conjugated diene monomer and allowing polymerization to occur, to produce a conjugated diene block;

(d) charging a randomizer, an initiator, and a conjugated diene/monovinylarene monomer mixture and allowing polymerization to occur, to produce a random (conjugated diene_x/monovinylarene_y)_m block;

(e) charging a conjugated diene monomer and allowing polymerization to occur, to produce a conjugated diene block; and

(f) charging the reaction mixture with a coupling agent, to form monovinylarene/conjugated diene block copolymer.

17. A monovinylarene/conjugated diene block copolymer, produced according to the method of claim 16.

18. A method of fabricating an article, comprising:

forming a monovinylarene/conjugated diene block copolymer into the article, wherein the monovinylarene/conjugated diene block copolymer comprises (i) a random (conjugated diene_x/monovinylarene_y)_m block, wherein x is about 2.5 wt% to about 10 wt%, y is from about 90 wt% to about 97.5 wt%, and x + y is about 97.5 wt% to 100 wt%; and (ii) a (conjugated diene)_n block; wherein n is from about 20 wt% to about 30

wt%, m is from about 70 wt% to about 80 wt%, and m + n is from about 90 wt% to 100 wt%.

19. The method of claim 18, wherein forming comprises sheet extrusion,
5 thermoforming, injection molding, blow molding, film blowing, or film casting.
20. A monovinylarene/conjugated diene block copolymer, comprising the structure:
(B/S)-B-CA,
wherein (B/S) is a random monovinylarene/conjugated diene block; B is a
10 conjugated diene block; CA is a coupling agent residue; and - is a covalent linkage
between blocks.
21. The monovinylarene/conjugated diene block copolymer of claim 20, further
comprising a second (B/S) block covalently linked to the (B/S) block of the (B/S)-B-CA
15 structure.
22. The monovinylarene/conjugated diene block copolymer of claim 20, further
comprising a second (B/S)-(B/S)-B structure covalently linked to the (B/S) block of the
(B/S)-B-CA structure.
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23. The monovinylarene/conjugated diene block copolymer of claim 20, further
comprising a second (B/S)-B structure covalently linked to the (B/S) block of the (B/S)-
B-CA structure.
24. The monovinylarene/conjugated diene block copolymer of claim 20, further
comprising a second S-(B/S)-B- structure covalently linked to the (B/S) block of the
(B/S)-B-CA structure, wherein S is a monovinylarene block.
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25. A monovinylarene/conjugated diene block copolymer, comprising the structure:
30 <B/S>²-<B/S>³-<B/S>⁴-<B/S>⁵-CA,

wherein <B/S> is a tapered monovinylarene/conjugated diene block; <B/S>2 has a conjugated diene content from about 2.5 wt% to about 10 wt%, and <B/S>3, <B/S>4, and <B/S>5 have a conjugated diene content from about 30 wt% to about 70 wt%.

5 26. The monovinylarene/conjugated diene block copolymer of claim 25, further comprising a <B/S>1 block covalently linked to the <B/S>2 block of the <B/S>2-<B/S>3-<B/S>4-<B/S>5-CA structure, wherein <B/S>1 has a conjugated diene content from about 2.5 wt% to about 10 wt%.

10 27. A monovinylarene/conjugated diene block copolymer, comprising the structure:
(B/S)1-(B/S)2-<B/S>3-<B/S>4-<B/S>5-CA,
wherein (B/S) is a random monovinylarene/conjugated diene block; <B/S> is a tapered monovinylarene/conjugated diene block; CA is a coupling agent residue; - is a covalent linkage between blocks; (B/S)1 and (B/S)2 each have a conjugated diene content
15 from about 2.5 wt% to about 10 wt%; and <B/S>3, <B/S>4, and <B/S>5 each have a conjugated diene content from about 30 wt% to about 70 wt%.

28. A monovinylarene/conjugated diene block copolymer, comprising the structure:
(B/S)1-(B/S)2-(B/S)3-(B/S)4-(B/S)5-CA,
20 wherein (B/S) is a random monovinylarene/conjugated diene block; CA is a coupling agent residue; - is a covalent linkage between blocks; (B/S)1 and (B/S)2 each have a conjugated diene content from about 2.5 wt% to about 10 wt%; and (B/S)3, (B/S)4, and (B/S)5 each have a conjugated diene content from about 30 wt% to about 70 wt%.

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